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III. *Conclusion of the Experiments and Observations concerning the Attractive Powers of the Mineral Acids.* By Richard Kirwan, Esq. F. R. S.

Read Dec. 12, 1782.

HAVING found, as exactly as I was able, the quantity of each of the mineral acids taken up at the point of saturation by alkalies and earths, and also that taken up by phlogiston, when these acids are by it converted into an aërial form, I next endeavoured to find how much of these acids was taken up at the point of saturation by each of the metallic substances, and for this purpose procured the most saturated solution possible of each metallic substance soluble in any of these acids. These solutions did not, indeed, immediately answer my purpose, as they constantly retained an excess of acid; yet as they were the foundation of my subsequent observations, and as the experiments themselves are in many respects useful to be known, I shall here briefly relate their result, and confine myself to those circumstances singly that relate to my future investigations, or that have not heretofore been satisfactorily explained. The acids I used were dephlogisticated so far as to be colourless; the metals were for the most part very fine filings, or reduced in a mortar to a fine powder. They were added little by little to their respective menstruums, much more being thus dissolved than if the whole was thrown in at once; and the solution was performed in glass phials with bent tubes.

*Solution*

*Solution of iron in the vitriolic acid.*

100 grs. of bar-iron, in the temperature of  $56^{\circ}$ , require for their solution, 190 grs. of real acid, whose proportion to that of the water with which it should be diluted, is as 1 to 8, 10, or 12. It would act on iron, though its proportion were greater or lesser, but not so vigourously. If towards the end a heat of  $200^{\circ}$  were applied, 123 grs. of real acid would be sufficient.

The air produced by this solution is intirely inflammable, and generally amounts to 155 cubic inches.

Iron is also soluble with the assistance of a strong heat, and in smaller quantity in concentrated vitriolic acid; and in this case scarce any inflammable air is produced, but a large quantity of vitriolic air as Dr. PRIESTLEY has observed, and a small quantity of sulphur sublimes at the latter end. This fact is a clear refutation of Mr. LAVOISIER's hypothesis; for is it not evident, that the same substance which, when a dilute acid is used, goes off in the form of inflammable air, does when a concentrated acid is used, to unite this acid, and thus form both vitriolic air and sulphur? In the first case it cannot unite to the acid, by reason of the large quantity of water combined with the acid; and as the liquor, being mostly aqueous, contains a large quantity of specific fire, it receives that fire when the acid unites to the metallic earth, and flies off in the form of air. But in the second case, the concentrated acid, containing much less specific fire, cannot expel the phlogiston in the form of inflammable air (as this air absorbs a vast quantity of fire) but unites to it, when by heat it is further stripped of its water, and thus forms both

vitriolic air and sulphur. 100 grs. of iron, dissolved without heat, afford upwards of 400 of vitriol.

100 grs. of the vitriol crystallized contain 25 of iron, 20 of real acid, and 55 of water. When calcined nearly to redness these crystals lose about 40 of water.

The calces of iron are more or less soluble in this acid according to their degree of dephlogistication. Those that are phlogisticated (as that recently precipitated from a solution of vitriol by fixed alkalies) are also most soluble, and upon evaporation afford crystals, though paler than those formed of genuine iron. Those that are least phlogisticated are also least soluble, that is, require more real acid for their solution, and afford no crystals, but only a magma or mother liquor. Hence also, solutions of iron newly made diminish, and consequently phlogisticate the super-incumbent air, and consequently gradually emit phlogiston: and hence the calx, being more dephlogisticated, gradually falls unless more acid be added to keep it in solution.

#### *Iron in the nitrous acid.*

100 grs. of iron, to be perfectly dissolved, and not barely calcined, require 142 grs. of real nitrous acid, so diluted as that its proportion to water should be as 1 to 13 or 14; and when this last proportion is used, the heat of a candle may be applied for a few seconds, and the access of common air prevented. In this case not above 18 cubic inches of nitrous air are produced, all the rest is absorbed by the solution, and no red vapours appear. But if the proportion of acid and water be as 1 to 8 or 10, and heat be applied, a much greater quantity of iron will be dephlogisticated, though very little of it be held in solution; and by this means I have obtained from 100 grs. of iron, 83,87 cubic inches

of nitrous air; and by distilling the solution a still greater quantity may be obtained, which was absorbed by the solution. No inflammable air is obtained from solutions of iron or any other metallic substance in the nitrous acid, because this acid has less affinity to water, and more to phlogiston, than the vitriolic acid, and also contains much less fire than either the vitriolic or marine acids, as will be seen in the sequel, and therefore unites to phlogiston instead of barely expelling it. And hence it is, that the vitriolic acid, though united with 30 times its weight of water, will still visibly act on iron, and separate inflammable air in the temperature of  $55^{\circ}$ ; whereas nitrous acid, diluted with 15 times its weight of water, will have no visible effect on iron in that temperature.

The calces of iron, if not too much dephlogisticated, are also soluble, though difficultly, in the nitrous acid.

#### *Iron in the marine acid.*

100 grs. of iron require 215 of real marine acid for their solution. The proportion of acid to that of water in the spirit of salt I used was as 1 to 4. When it is as 1 to 4, it effervesces too violently. Heat is rather prejudicial, as it volatilises the acid. No marine air flies off, and the quantity of inflammable air is just the same as if dilute vitriolic acid were used.

The calces of iron are also soluble in marine acid. They may be distinguished from genuine iron in this, that their colour, when precipitated by fixed alkalies, is *reddish*, whereas the precipitate of genuine iron is *greenish*.

#### *Copper in the vitriolic acid.*

100 grs. of copper require nearly 183 grs. real vitriolic acid for their solution. The proportion of acid to that of water  
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being as 1 to  $\frac{1}{2}$ , or at least as 1 to  $\frac{7}{16}$ , and a strong heat must also be applied. I could never dissolve the whole of any quantity of copper; but to dissolve a given quantity of it, a still greater must be used in the proportion of nearly 28 to 100, though this residuum also is soluble by adding more acid. When copper has been dephlogisticated in this manner, a solution of it is obtained by adding warm water to the dephlogisticated mass.

The dephlogistication of 128 grs. of copper treated in this manner affords 11 cubic inches of inflammable air, and nearly 65 of vitriolic air. When I obtained inflammable the acid was a little more aqueous. The reason why copper cannot be dephlogisticated by dilute vitriolic acid, nor even by the concentrated, without the assistance of a strong heat, as iron is, appears derivable from its much stronger attraction to phlogiston, and the much greater quantity of it which copper contains, as will hereafter be seen. Hence

100 grs. of vitriol of copper contain 27 of copper, 30 of acid, and 43 of water, of which it loses about 28 by evaporation or slight calcination.

The solution of 100 grs. of copper affords 373 of blue vitriol.

### *Copper in nitrous acid.*

100 grs. of copper require 130 of real nitrous acid to dissolve them. If the acid be so far diluted as that its proportion to that of water be as 1 to 14, the assistance of heat will be necessary, otherwise not. This solution affords  $67\frac{1}{2}$  cubic inches of nitrous air.

The calces of copper are also soluble in this acid.

*Copper in marine acid.*

100 grs. of copper require 1190 grs. of real marine acid to dissolve them, and also the assistance of a moderate heat, the proportion of acid to that of water being as 1 to  $4\frac{1}{3}$ , that is, its specific gravity being 1,186, if a greater heat be used, more of the acid will be requisite, as much will be dissipated. If the acid be more concentrated, it will act more vigorously.

In my last paper I mentioned, that  $8\frac{1}{2}$  grs. of copper afforded 86 of marine air: however, I must now add a circumstance which I then did not attend to, which is, that the mercury over which that air was received was acted upon, so that part of the air was due to this action, which invalidates the conclusion I there drew concerning the quantity of phlogiston in marine air, which hence appears to be greater than I there estimated it.

The calces of copper are also soluble in this acid, though not so easily as in the nitrous acid.

*Tin in the vitriolic acid.*

100 grs. of tin require for their perfect solution 872 grs. of real vitriolic acid, whose proportion to water should not be less than as 1 to  $\frac{9}{16}$ , and also the assistance of a strong heat; when the action of the acid has ceased, some hot water should be added to the turbid solution, and the whole again heated. This solution affords 70 cubic inches of inflammable air. Tin is also soluble in a more dilute acid, but not in so great quantity.

The calces of tin (except that precipitated from marine acid by fixed alkalies) are insoluble in this acid.

*Tin*

*Tin in the nitrous acid.*

100 grs. of tin require, for their perfect solution, 1200 grs. of real nitrous acid, whose proportion to water should be at least as 1 to 25, and the heat not exceeding  $60^{\circ}$ : the quantity of air afforded by such solution is only ten cubic inches, and it is not nitrous. The solution is not permanent; for in a few days it deposits a whitish calx, and if the weather be warm bursts the phial. The calces of tin are insoluble in this acid.

*Tin in the marine acid.*

100 grs. of tin require for their solution 413 of real marine acid, whose proportion to water is as 1 to  $4\frac{1}{2}$ , and also the assistance of a moderate heat. This solution affords about 90 cubic inches of inflammable air and 10 of marine air. The calces of tin are nearly insoluble in this acid.

*Lead in the vitriolic acid.*

100 grs. of lead require for their solution 600 grs. of real acid, whose proportion to water is not less than that of 1 to  $\frac{7}{10}$ , and better if the quantity of water be still less; and hence, as with regard to copper, a greater quantity of lead should be employed than is expected to be dissolved. A strong heat is also requisite, and hot water should be added to the calcined mass, though sparingly, as it occasions some precipitation.

This metal is also soluble, but in a very small degree, in dilute vitriolic acid; for it effervesces with spirit of vitriol whose specific gravity is only 1,275.

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The calces of lead are something more soluble in this acid. 100 grs. of vitriol of lead, formed by precipitation, contains 73 of lead, 17 of real acid, and 10 of water. Vitriol of lead, formed by direct solution, contains a large proportion of acid.

*Lead in the nitrous acid.*

100 grs. of lead require for their solution about 78 grs. of real acid, whose proportion to that of water may be as 1 to 11 or 12, and the assistance of heat towards the end. This solution affords but eight cubic inches of nitrous air. The calces of lead are also soluble in this acid; but if much dephlogistified they become less soluble.

100 grs. of minium require 81 grs. of real acid.

100 grs. of nitrous salt of lead contain about 60 of lead.

*Lead in the marine acid.*

100 grs. of lead require 600 grs. of real acid to dissolve them, when the specific gravity of the spirit of salt is 1,141, and also the assistance of heat, by which much of the acid is dissipated. A stronger acid would dissolve more.

The calces of lead are more soluble in this acid than genuine lead. 100 grs. minium require 327 grs. of real acid; but white lead is much less soluble.

100 grs. of horn lead, formed by precipitation, contain 72 of lead, 18 of marine acid, and 10 of water.

*Silver in the vitriolic acid.*

100 grs. of pure silver require to dissolve them 530 grs. of real vitriolic acid, whose proportion to water is not less than that of 1 to  $\frac{3}{16}$ , and when such a concentrated acid is used, it acts slightly even in the temperature of 60°; but for a copious solution

folution a moderate heat is requisite. This folution affords 30 cubic inches of vitriolic air. Standard filver affords more air and requires more acid for its folution. The calces of filver (that is, filver precipitated from its folution in nitrous acid by fixed alkalies, and well-washed, but which ftill retains fome nitrous acid), are foluble even in dilute vitriolic acid, without the affiftance of heat. 100 grs. of vitriol of filver, formed by precipitation, contain 74 grs. of filver, about 17 of real acid, and 9 of water.

*Silver in the nitrous acid.*

100 grs. of the pureft filver require for their folution 36 of mere nitrous acid, diluted with water in the proportion of one part real acid to 6 of water, applying heat only when the folution is almoft faturate. If fpirit of nitre be much more or much lefs dilute, it will not act without the affiftance of heat. The laft portions of filver, thus taken up, afford no air. *Standard* filver requires about 38 grs. of real acid to diffolve the fame proportion of it. And the folution of it affords 20 cubic inches of nitrous air, whereas 100 grs. of filver, revived from *luna cornua*, afford about 14.

*Silver in the marine acid.*

I have not been able to diffolve filver, in its metallic ftate, in fpirit of falt, yet I believe it may be effected, if fufficient time be allowed, as Mr. BAYEN, in his Treatife on Tin, p. 201. fays, he diffolved  $3\frac{1}{2}$  grs. of filver by digefting it for fome days in two ounces of ftrong fpirit of falt. Leaf filver is alfo faid to be corroded by ftrong fpirit of falt, 1 NEWM. 70. The dephlogifticated marine acid alfo diffolves it, according to the obfervations of Mefl. SCHEELE and BERGMAN: and fo does the phlogifticated

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cated in a vaporous state. 100 grs. of horn silver contain 75  
of silver; nearly 18 of acid, and 7 of water.

*Gold in aqua regia.*

I made several experiments with aqua regia, in which the nitrous and marine acids were mixed in different proportions, and found *that* to succeed best, in which the quantity of real marine acid was to that of the nitrous as 3 to 1, and both as concentrated as possible; though if both be very concentrated, it is hard to mix them so as to prevent a great quantity from escaping, as they effervesce very violently some time after mixture. 100 grs. of gold require 246 grs. real acid for their solution, the two acids being in the above mentioned proportion.

The specific gravity of the nitrous acid I used was 1,465, and that of the marine 1,178. The solution is better promoted by allowing it sufficient time than by applying heat. The heat I used did not exceed 90 or 100°. Very little air is produced, and the solution is very slow. Aqua regia made with common salt or sal ammoniac and spirit of nitre is much less aqueous, than that resulting from an immediate combination of both acids; and hence is the fittest for the production of crystals of gold.

Gold is also soluble in the dephlogisticated marine acid, but in very small quantity, unless this acid be in a vaporous state, for in a liquid state it is too aqueous. In vitriolic and nitrous acids it is also insoluble; but the calces of gold are easily soluble in the marine acid, very slightly in the nitrous, and scarce at all in the vitriolic. Gold in its metallic state may be diffused through, but not dissolved, by the concentrated nitrous acid.

*Mercury in vitriolic acid.*

100 grs. of quicksilver require for their solution 230 grs. of real vitriolic acid, whose proportion to that of water is at least as 1 to  $\frac{8}{10}$ , and also a strong heat. The air produced is vitriolic. Precipitate, *per se*, is still less soluble.

100 grs. of vitriol of mercury, produced by precipitation, contain 77 of mercury, 19 of acid, and 4 of water.

*Mercury in nitrous acid.*

100 grs. of mercury are dissolved by 28 grs. of real nitrous acid, whose proportion to that of water is as 1 to 1 and  $\frac{5}{100}$ , and without the assistance of heat. Mercury is also soluble, but in smaller quantity, in a much more dilute acid, with the assistance of heat. The product of air is about 12 cubic inches or less, if heat be not applied. Mr. LAVOISIER found the product of air much greater, which evidently was caused by his using red or yellow spirit of nitre, which already contains much phlogiston. When I dissolved a hundred grs. of mercury in three times more acid than was necessary for its solution, and without heat, I obtained but 7 cubic inches of nitrous air, and the solution was green; but, on applying heat when the solution was over, I obtained 2 more cubic inches, and then the solution was of the colour of oil of olives.

Precipitate, *per se*, is much more difficultly dissolved by nitrous acid than genuine mercury, which I attribute to the attraction of the aerial acid contained in the precipitate.

*Mercury in marine acid.*

The marine acid, in its common phlogisticated state, does not act on mercury, at least in its usual state of concentration;

but Mr. HOMBERG, in the Paris Memoirs for the year 1700, assures us, he dissolved mercury in marine acid, whose specific gravity was 1,300, by keeping it some months in digestion. The authors of the *Cours de Chymie de Dijon* affirm also its solubility in this acid, though in very small quantity. The dephlogistified marine acid, in a vapourous state, certainly acts upon it, though while in a liquid state it is too weak, by reason of its dilution.

Precipitate, *per se*, is also soluble in marine acid, with the assistance of heat. 100 grs. of sublimate corrosive contain 77 of mercury, 16 of real acid, and 6 of water. 100 grs. of mercurius dulcis contain 86 of mercury, and 14 of acid and water.

#### *Zinc in vitriolic acid.*

100 grs. of zinc require for their solution 100 grs. of real acid, whose proportion to that of water may be as 1 to 8, 10, or 12, applying heat towards the end, when the acid is almost saturated. A small quantity of black powder always remains undissolved. The product of inflammable air is 100 cubic inches. It is soluble in the concentrated vitriolic acid, with the aid of heat.

100 grs. of vitriol of zinc contain 20 of zinc, 22 of acid, and 58 of water.

The calces of zinc, if not exceedingly dephlogistified, are also soluble in this acid.

#### *Zinc in nitrous acid.*

100 grs. of zinc require for their solution 125 grs. of real nitrous acid, whose proportion to that of water is as 1 to 12, applying from time to time a slight heat. If a concentrated acid

be used, less will be dissolved, as much of the acid will escape during the effervescence. I could procure no nitrous air from the solution by any management, as the nitrous acid is in part decomposed during the operation.

The calces of zinc, if not too much dephlogisticated, are also soluble in this acid.

*Zinc in Marine Acid.*

The same quantity of zinc requires of this acid 210 grs. the proportion of real acid in the menstruum being as 1 to 9, and using from time to time a slight heat. If a less dilute acid be used, more real acid will be requisite, as much of it will escape during the effervescence.

The calces of zinc are also soluble in this acid.

*Bismuth in vitriolic acid.*

200 grs. of oil of vitriol, whose specific gravity was 1,863, dissolved but three grs. of wismuth in a strong heat; but slightly dephlogisticated a greater quantity. 400 grs. of spirit of vitriol, whose specific gravity was 1,200, dissolved but one grain. The calces of wismuth are much more soluble. The solution of the 3 grs. afforded 4 cubic inches of vitriolic air.

*Bismuth in nitrous acid.*

The solution of 100 grs. of bismuth require but 100 grs. of real nitrous acid, whose proportion to water should be as 1 to 8 or 9. In this last case, a gentle heat may be applied. This solution affords 44 cubic inches of nitrous air. The calces of bismuth are also soluble in this acid.

*Bismuth in marine acid.*

400 grs. of spirit of salt, whose specific gravity is 1,220, dissolved only 3 or 4 grs. of bismuth.

*Nickel in vitriolic acid.*

100 grs. of concentrated vitriolic acid dissolve about 4 of nickel, with the assistance of a strong heat. The calces of nickel are much more soluble.

*Nickel in nitrous acid.*

100 grs. of nickel require for their solution 112 grs. of nitrous acid, whose proportion to water is as 1 to 11 or 12, assisted with a moderate heat. A concentrated acid acts so rapidly that much is dissipated. The product of nitrous air is 79 cubic inches. The calces of nickel are also soluble in this acid.

*Nickel in marine acid.*

200 grs. of spirit of salt, whose specific gravity is 1,220, dissolved 4 or 5 grs. of nickel, without the assistance of heat. A weaker acid dissolves less, and requires the assistance of heat. In all these cases of difficult solution more of the metal will be taken up by distillation and cohobation ; but the proportion will be difficult to assign.

The calces of nickel are also difficultly soluble in this acid.

*Cobalt in vitriolic acid.*

100 grs. of cobalt require 450 grs. of real acid, whose proportion to its water is not less than 1 to  $\frac{7}{16}$ , and a heat of

270° at least. By pouring warm water on the dephlogisticated mass a solution is obtained.

The calces of cobalt are still more soluble; even a dilute acid will serve.

*Cobalt in nitrous acid.*

100 grs. of cobalt requires 220 grs. of real nitrous acid, whose proportion to water is as 1 to 4, giving towards the end a heat of 180°.

The calces of cobalt are soluble in this acid.

*Cobalt in marine acid.*

100 grs. of spirit of salt, whose specific gravity is 1,178, dissolves, with the assistance of heat, 2½ grs. of cobalt. A more concentrated acid will dissolve more.

The calces of cobalt are more soluble in this acid.

*Regulus of antimony in vitriolic acid.*

100 grs. of regulus of antimony require for their solution 725 grs. of real acid, whose proportion to water is as 1 to  $\frac{7}{16}$ , and a heat of 400°. More regulus should be employed than is expected to be dissolved, and the resulting salt requires a large quantity of water to dissolve it; for the concentrated acid lets fall much when water is added to it. A less concentrated acid will also dissolve this semi-metal, but in smaller quantity.

The calces of antimony, even diaphoretic antimony, are something more soluble.

*Regulus of antimony in nitrous acid.*

100 grs. of this semi-metal require 900 grs. of real nitrous acid, whose proportion to water is as 1 to 12, aided with a heat



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heat of  $110^{\circ}$ . The solution, however, becomes turbid in a few days.

The calces of antimony are soluble in a much less degree.

*Regulus of antimony in marine acid.*

100 grs. of spirit of salt, whose specific gravity is 1,220, dissolve about 1 gr. of regulus, with the assistance of a slight heat. Spirit of salt, whose specific gravity is 1,178, also acts upon it, but dissolves still less. I believe the concentrated acid would, in a long time, and with the help of a gentle heat, dissolve much more of it.

The calces of antimony are much more soluble in this acid.

*Regulus of arsenic in vitriolic acid.*

200 grs. of oil of vitriol, whose specific gravity is 1,871, dissolve 18 of regulus of arsenic in a heat of  $250^{\circ}$ . Of these about 7 crystallize on cooling, and are soluble in a large quantity of water.

The calces of arsenic are more soluble in this acid.

*Regulus of arsenic in nitrous acid.*

100 grs. of this semi-metal require 140 grs. of real nitrous acid, whose proportion to water is as 1 to 11, and the assistance of heat. It is soluble in a less or more concentrated acid, but in a lesser degree. This solution affords 102 cubic inches of nitrous air. The barometer at 30, and the thermometer at 60.

The calces of arsenic are also soluble in this acid.

*Regulus of arsenic in marine acid.*

100 grs. of spirit of salt, whose specific gravity is 1,220, dissolve  $1\frac{1}{2}$  grs. of regulus of arsenic; the marine acid, in its  
common

common dilute state, that is, whose specific gravity is under 1,17, does not at all affect it.

The calces of arsenic are less soluble in this acid than in the vitriolic or nitrous.

We have now gone through most of the bases to which acids are capable of uniting (manganese and platina I have purposely omitted, as I was not possessed of a sufficient quantity of either in that degree of purity requisite for exact experiments). We have also seen the quantity of the mineral acids requisite to saturate each basis, except the metallic bases, all of which require an excess of acid, not only to dissolve them, as in most cases much of it flies off with the phlogiston in an aerial form, but also to keep them in solution. The quantity of any basis, taken up by a given quantity of any of these acids, is easily found; for if 100 grs. of any basis take up, at the point of saturation, or require for their solution, the quantity *a* of any acid, the quantity taken up or dissolved by 100 grs. of that acid will be  $\frac{10000}{a}$ .

The proportion of ingredients which I have assigned to different neutral salts appears, at first sight, very different from that which Mr. BERGMAN has ascribed to them. This for some time made me very uneasy, as I have the highest confidence in the skill and judgement of that excellent chymist; but on a strict examination I have found, that the difference is more apparent than real. Mr. BERGMAN has never attempted to ascertain the quantity of *real* acid in any substance; but has, according to the custom of all preceding writers, bestowed the title of *acid* on those liquids which contain it in the most concentrated, or at least in a very concentrated state, but which

still confessedly contain some undetermined proportion of water, and by the quantity of water he commonly understands that which is retained by crystallization: thus, in his first vol. p. 137. he says, that 100 grs. of vitriol of iron contain 23 of iron, 39 of vitriolic acid, and 38 of water. But in his treatise *De Productis Vulcanicis*, § 12. he says, that 100 grs. of vitriol of iron contain 24 of iron, 24 of *dephlegmated* vitriolic acid, and 52 of water; and this last calculation scarcely differs from mine, as I assign to 100 grs. of vitriol 25 of iron, 20 of real vitriolic acid, and 55 of water. The difference manifestly arises from the quantity of water still contained in his dephlegmated acid. The most material difference between us regards the quantity of the mineral acids taken up by alkalies; for, according to his and Mr. SCHEFFER's experiments, they take up more of the vitriolic than of the nitrous, and more of the nitrous than of the marine; whereas, according to Mr. HOMBERG's, Dr. PLUMMER's, Mr. WENZEL's, and my experiments, this does not happen. This difference arises in all probability from the different degrees of evaporation by which the crystals of these salts are obtained; for which reason I did not examine the quantity of the crystals, which must be variable, but that of dry salt, left after thorough evaporation. With regard to the quantity of earth and metallic basis in different salts, Mr. BERGMAN's experiments and mine agree almost entirely.

The advantages resulting from these inquiries are very considerable, not only in promoting chymical science, which, being a physical analysis of bodies, essentially requires an exact determination, as well of the quantity and proportion, as of the quality of the constituent parts of bodies, but also in the practical way. Thus, in the first place, it is well known, that  
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Several important processes are very inaccurately described by ancient chymical writers, and even by some of a modern date, they frequently, for instance, describe the acid they employed by reference to the quantity of fixed alkali, earth, or metal, a given quantity of such acid was capable of neutralizing or dissolving. Now the foregoing observations immediately inform us of the quantity of real acid capable of performing that effect; the remainder, therefore, must have been water; and the quantity of real acid and water being known, the specific gravity is easily found by the help of the foregoing tables, and thus an acid of the same strength may be formed. Thus SCHLUTTER, in the best treatise on *Essaying yet extant*\*, informs us, that the best aqua fortis for parting silver from gold is that of which a pound dissolves one mark, that is, half a pound of silver: then 1000 grs. of it should dissolve 500 of silver. Now, by the foregoing experiments, we find, that 100 grs. of alloyed silver require 38 of real acid for their solution; consequently 500 grs. of silver will require 190 grs.; consequently 1000 grs. of such spirit of nitre should contain 190 grs. of real acid and 810 of water. Then recurring to the table of the nitrous acid, I find, by the rule of proportion, that the specific gravity of this acid must be about 1,261; for as 190 is to 810, so is 393 acid to 1675 of water. This proportion of water is somewhat greater than that I used, but SCHLUTTER uses a sand heat.

2dly, The importance of this knowledge in the art of pharmacy is very obvious, especially with regard to medicines formed of metallic substances, whose powers depend on the proportion of their ingredients, and their action on each other.

3dly, This degree of precision must tend considerably to the

\* Vol. I. p. 332. French edition.

improvement of the arts of dying and enamelling, the processes by which many of their ingredients are procured being at present much too vague. Thus the process at present used for preparing the precipitate of CASSIUS frequently fails, the strength of the acids not being sufficiently ascertained.

4thly, The uses of this knowledge in the examination of mineral waters, and in assaying of ores, have been amply proved in the elaborate treatises which the celebrated BERGMAN has lately given us on these subjects. And I may further add, that the knowledge of the quantity of acid requisite for the solution of different metallic substances may also furnish us with a new criterion for distinguishing them from each other, and the purer from their alloys, and in some cases inform us of the quantity and quality of the alloy: thus, 100 parts pure silver require less of the nitrous acid to dissolve them than 100 grs. of standard silver; thus also, by dissolving in spirit of salt any metallic substance sufficiently soluble therein, we may know whether it contains the smallest particle of silver, quicksilver, or arsenic, as these are almost insoluble therein, or of regulus of antimony, cobalt, nickel, or wismuth, of which it also takes but a small proportion.

But the end which of late I had principally in view, was to ascertain and measure the degrees of affinity or attraction that subsist betwixt the mineral acids, and the various bases with which they may be combined, a subject of the greatest importance, as it is upon this foundation that chymistry, considered as a science, must finally rest; and though much has been already done, and many general observations laid down on this head, yet so many exceptions have occurred even to such of these observations as seemed to have been most firmly established, that not only a variety of tables of affinity have been formed,

but many very eminent chymists have been induced to doubt, whether any general law whatsoever could be traced. But, as the judicious BERGMAN well observes, it were much more reasonable to examine the circumstances of these exceptions, which undoubtedly arise from the introduction of new powers, and lay down rules qualified with such restrictions as are observed in the action of these antagonist powers. This is the plan I have followed; but before I proceed to explain myself, I must open the subject in a more general way.

Chymical affinity or attraction is that power by which the invisible particles of different bodies intermix and unite with each other so intimately as to be inseparable by mere mechanical means. In this respect it differs from magnetic and electrical attraction. It also differs from attraction of cohesion in this, that the latter takes place betwixt particles of almost all sorts of bodies whose surfaces are brought into immediate contact with each other; for chymical attraction does not act with that degree of indifference, but causes a body already united to another to quit that other and unite with a third, and hence it is called *elective* attraction. Hence attraction of cohesion often takes place betwixt bodies that have no chymical attraction to each other; thus regulus of cobalt and wismuth have no chymical attraction to each other, for they will not unite in fusion, yet they cohere with each other so strongly, that they can be separated only by a stroke of a hammer.

Hence bodies, which refuse to unite to each other chymically when they are most minutely divided, as when both are in a vaporous or aerial state, or when both are in a liquid state, may be judged, in the first case, to have none; or in the second case, to have at best but a very small affinity to each other. But those that unite, when one of them only is in a liquid state,

may be said to have a strong affinity to each other, and it is thus that acids unite to alkalies, earths, and metals, for the most part.

In order to determine the degrees of affinity, Mr. GEOFFROY has laid it down as a general rule, that when two substances are united, and either quits the other to unite to a third, that which thus unites to this third substance must be said to have a greater affinity to it than to the substance it has quitted. This undoubtedly is the case when only two attractive powers are concerned; thus, when selenite is decomposed by a caustic fixed alkali, it is evident, that the vitriolic acid has a stronger affinity to the alkali than to the earth; but in many cases a decomposition, seemingly single, is in fact double, and the result of the action of more than two powers, and then it is not easy to know which is the greatest, nor consequently to determine the degree of attraction; for instance, the vitriolic acid unites to a mild fixed alkali, and expels the fixed air from it, yet it does not necessarily follow, that the vitriolic acid attracts, or is attracted, by the alkali more strongly than the ærial acid; for though there appears here only a single decomposition, yet in reality a sort of double decomposition takes place, the vitriolic acid giving out its fire to the ærial, while the ærial resigns the alkali to the vitriolic; and hence a decomposition might well take place, even on the supposition that the affinity of both acids to the alkali was equal: therefore, to attain any certainty in this matter, it is necessary to ascertain the quantity and force of each of the attractive powers, and denote it by numbers.

Mr. MORVEAU was the first who perceived the necessity of this calculation, and he has accordingly communicated to us, in numbers, a table of the attractive power of mercury with respect to metals; but his method is incapable of being genera-

lized. Mr. WENZEL had also an eye to such calculation; but his method is much more defective. It is only this, “ To discover (says he) the quantity of affinity which the nitrous acid bears to the different substances with which it is capable of uniting, let small equal cylinders of each of the metals be covered over, except at one end, with melted amber, and then exposed to equal quantities of the same spirit of nitre, and in the same temperature; then let the times of the solution of each be noted. *The affinity of the acid to each of these metals will be inversely as the times necessary for the solution of equal quantities of them.*” And as he well knew that spirit of nitre, of the same degree of concentration, would not act equally on each of them, he required that it should be diluted in some cases, and undiluted in others, and allowance to be made for this in the subsequent calculation. But alkalies and earths are here intirely omitted; and even as to metals no conclusion can be drawn by this method. Tin and regulus of antimony are most rapidly attacked by this acid, lead and copper much more slowly; yet it is well known, that its affinity to lead is much stronger than its affinity to tin, and its affinity to copper greater than to regulus of antimony. Silver and quicksilver are more slowly dissolved, and yet the affinity of the nitrous acid to these metals, as will be seen in the sequel, is by far the greatest.

Neither can this method be in any wise applied to the estimation of the affinities of the other mineral acids; for though the vitriolic and marine acids dissolve very slowly, difficultly, and sparingly, several metals that are copiously and readily dissolved by the nitrous, yet they both have a stronger affinity to those very metals than the nitrous has to them, as is evident with regard to silver, mercury, and lead, which are precipitated from the  
nitrous



nitrous by the vitriolic and marine, though the two first are insoluble in the marine, and all three difficultly soluble in the vitriolic. Accordingly, we do not find that Mr. WENZEL has ever made the proposed experiments, at least he makes no mention of their result.

The discovery of the quantity of real acid in each of the mineral acid liquors, and the proportion of real acid, taken up by a given quantity of each basis at the point of saturation, led me unexpectedly to what seems to me the true method of investigating the quantity of attraction which each acid bears to the several bases to which it is capable of uniting; for it was impossible not to perceive,

First, That *the quantity of real acid, necessary to saturate a given weight of each basis, is inversely as the affinity of each basis to such acid.*

Secondly, That *the quantity of each basis, requisite to saturate a given quantity of each acid, is directly as the affinity of such acid to each basis.*

Thus 100 grs. of each of the acids require for their saturation a greater quantity of fixed alkali than of calcareous earths, more of this earth than of volatile alkali, more of this alkali than of magnesia, and more of magnesia than of earth of allum, as may be seen in the following table.

*Quantity of basis taken up by 100 grs. of each of the mineral acids.*

	Veg fixed alkali. Grs.	Min. alkali. Grs.	Calcar. earth. Grs.	Vol. alkali. Grs.	Mag- nesia. Grs.	Earth of allum. Grs.
Vitriolic acid	215	165	110	90	80	75
Nitrous acid	215	165	96	87	75	65
Marine acid	215	158	89	79	71	55

As

As these numbers agree with what common experience teaches us concerning the affinity of these acids with their respective bases, they may be considered as adequate expressions of the quantity of that affinity, and I shall in future use them as such. Thus the affinity of the vitriolic acid to fixed vegetable alkali, that is, the force with which they unite, or tend to unite, to each other, is to the affinity with which that same acid unites to calcareous earth as 215 grs. to 110; and to that which the nitrous acid bears to calcareous earth as 215 grs. to 96, &c. But before I proceed further in the comparison of these forces, it is necessary to say something of the nature of *saturation*.

A body is said to be *saturated* with another, when it is so intimately combined with that other as to lose some peculiar characteristic property, which it possesses when free from that other. Thus acids possess the property of changing the juice of turnsol, or infusion of litmus, *red*. According to Mr. BERGMAN one grain of the most concentrated oil of vitriol will give a visible redness to 172,300 grs. of this infusion, and one cubic inch of water, saturated with fixed air (the weakest of all acids, as is generally thought) of which water takes up only about its own bulk, and consequently 253 grs. take up only about half a grain, reddens 50 cubic inches, that is, about 12,650 grs. of the infusion. When acids lose this property they are said to be saturated: and if both bodies are saturated, the compound is said to be *neutralized*.

If an acid be united to less of any basis than is requisite for its saturation, its affinity to the deficient part of its basis is as the ratio which that deficient part bears to the whole of what the acid can saturate. Thus if 100 grs. of vitriolic acid be united to 55 parts only of calcareous earth, its affinity to the deficient

55 parts

55 parts should be estimated half of its whole affinity, as 55 is the half of 110; but its affinity to the retained part is as its whole affinity.

I shall now shew how all decompositions, in which these three acids and the above mentioned bases are alone concerned, may easily be explained.

In all decompositions we must consider, first, the powers which resist any decomposition, and tend to keep the bodies in their present state; and, secondly, the powers which tend to effect a decomposition and a new union. The first I shall call *quiescent* affinities, and the second sort *divellent*.

A decomposition will always take place when the sum of the *divellent* affinities is greater than that of the *quiescent*; and, on the contrary, no decomposition will happen when the sum of the *quiescent* affinities is superior to, or equal to, that of the *divellent*: all we have to do, therefore, is to compare the sums of each of these powers. Thus, if the solutions of tartar vitriolate and nitrous selenite be mixed, a double decomposition will take place, a true selenite and nitre being the result of such mixture.

Quiescent affinities.		Divellent affinities.	
Vitriolic acid to fixed veget. alkali	215	Vitriolic acid to calcareous earth	110
Nitrous acid to calcareous earth	96	Nitrous Acid to vegetable alkali	215
Sum of the quiescent affinities	311	Sum of the divellent	325

Hence a double decomposition must necessarily happen.

The same double decomposition will be produced if, instead of tartar vitriolate, GLAUBER'S salt be used, 1 MARGR. 392; for the sum of the quiescent affinities is 261, and that of the *divellent* 275. So also, if *vitriolic ammon.* be used for the sum

of the quiescent is 186, and that of the divellent 195, or Epsom salt, 1 MARGR. 390. Mem. Par. 1778, p. 339. or *allum*, 1 MARGR. 387. The determinations, however, with regard to allum are not quite so exact as the foregoing; because allum, whether vitriolic, nitrous, or marine, constantly retains an excess of acid, the exact point of saturation cannot be found as I have already remarked, and is well known: however, the superiority is on the side of the divellent affinities, as it should be. If, instead of a solution of nitrous selenite, that of marine selenite be mixed with the solutions of the above mentioned vitriolico-neutral salts, the same sort of double decomposition will happen, and a true selenite will be formed, 1 MARGR. 382; and on calculation it will be constantly found, that the sum of the divellent constantly exceeds that of the quiescent affinities.

So also, if a solution of tartar vitriolate be mixed with a solution of nitrous or marine Epsom, a double decomposition will take place, though no visible change will appear in the mixed liquor, as vitriolic Epsom is exceeding soluble in water, and therefore is not precipitated as selenite is, on account of its insolubility, Mem. Par. 1778, p. 338. In the first case, the sum of the quiescent powers is 290, and of the divellent 295; in the second case, that of the quiescent is 286, and of the divellent 295.

If a solution of GLAUBER's salt be mixed with that of nitrous or marine Epsom, an invisible double decomposition will also happen, Mem. Par. *ibid.* Hence Mr. QUATREMERE DIJON-VAL, who lately denied this double decomposition (ROZ. Mai 1782, p. 392.) was certainly deceived. In the first case, the sum of the quiescent affinities is 240, and of the divellent 245; in the second case, that of the quiescent is 236, and of

the divellent 238. Further, if a solution of nitre be mixed with a solution of marine selenite, an invisible double decomposition will ensue, *Mem. Par.* 1778, p. 341.; the sum of the quiescent powers being 304, and of the divellent 313.

If a solution of nitrous Epsom be mixed with that of marine selenite, a double decomposition will be the consequence, 17 ROZ. 393.: the sum of the quiescent affinities being 164, and that of the divellent 167.

From all which I collect, first, that the quantity of each affinity, as here determined, perfectly coinciding with all the facts hitherto known, which are pretty numerous, may be looked upon as exact or nearly so. 2dly, That these decompositions are perfectly consistent with the superior affinity which hitherto has been generally ascribed to the vitriolic and nitrous acids with fixed alkalies over that which these acids bear to earths, and do not in the least infringe the received laws of affinities, as *Messrs. MARHER, MONNET, and lately Mr. CORNETTE*, in the *Memoirs of Paris* for 1778, p. 339. do insinuate.

There is a fact, however, in that valuable repository of chymical knowledge, *Mr. CRELL'S Chymical Journal*\*, which at first sight seems contrary to one of the above determinations; it is there said, that if solutions of one part allum and two parts common salt be mixed together, evaporated to a certain degree, and set to crystallize, a *GLAUBER'S* salt will be found; yet in this case the sum of the quiescent affinities is 233, and that of the divellent but 223. I repeated this experiment without success, and indeed the author owns it never succeeds but during the most intense cold.

If it does succeed at all, the decomposition must arise from a large excess of acid in the allum, which acted upon and de-

\* 6 THEIL. p. 78.

composed the common salt; and this explanation is confirmed by the small proportion of GLAUBER's salt, which is said to be obtained by this process; for from 30 lbs. of common salt and 16 lbs. of allum only, 15 lbs. of GLAUBER's salt were produced; whereas, if the whole of the allum were decomposed, there should be formed, according to my computation of the proportion of acid in different salts,  $29\frac{1}{2}$  lbs., and, according to Mr. BERGMAN's, 22 lbs. of GLAUBER's salt.

Besides these powers there exists another which neutral salts possess, of uniting to certain substances, without suffering any, or but a very small, decomposition; and thus forming *triple* salts, and sometimes quadruple. This often causes anomalies, and has not as yet been sufficiently investigated\*. Volatile alkalies in particular possess this power; and hence, perhaps, arises the difference between Mr. BERGMAN's table and mine, with regard to them and magnesia; for though, when perfectly caustic, they do not perfectly precipitate magnesia from Epsom salt, it is because they combine with this salt and form a triple salt.

According to my table, the three mineral acids have the same affinity to vegetable fixed alkalies, which will undoubtedly appear extraordinary to many, as it is well known, that the vitriolic acid decomposes both nitre and salt of sylvis; but it should be remarked, that tartar vitriolate is also decomposed by the nitrous and marine acids, as Mr. BAUMÉ, MARGRAAF, and BERGMAN, have found; and nitre is decomposed by the marine acid, as Mr. CORNETTE has shewn at large in the *Memoirs of Paris* for 1778; and not only these salts, but also GLAUBER's salt and vitriolic ammoniac, are decomposed by the

\* In my next paper I shall examine some exceptions arising from this source.

nitrous acid; and also these salts, together with cubic nitre and nitrous ammoniac, are decomposed by the marine acid, as Mr. BERGMAN and Mr. CORNETTE have remarked: all which shew, that these decompositions are the effect of a double affinity, or at least of compound forces. I always suspected they arose from the different capacities of these acids for elementary fire; but as the subject appeared to me of importance, for greater certainty I made a series of experiments which differ from those hitherto made in several respects, particularly in this, that no heat was applied, and the decompositions were discovered, not by crystallization, but by tests.

First, I procured equal weights of each of the mineral acids, containing each the same quantity of real acid; and throwing each suddenly on an ounce of the same oil of tartar, I had the following results, the temperature of all, before mixture, being  $68^{\circ}$  of FAHRENHEIT. 100 grs. of vitriolic acid, containing 26,6 grs. of real acid projected on 480 of oil of tartar, raised the thermometer to  $138^{\circ}$ .

100 grs. of spirit of nitre, which also contained 26,6 grs. real acid, projected in the same manner on 480 grs. of the same oil of tartar, produced a heat of  $120^{\circ}$ .

100 grs. of spirit of salt, whose specific gravity was 1,220, and which contained 26,6 grs. of real acid, projected on the above quantity of the same oil of tartar, raised the thermometer from 69 to  $129^{\circ}$ .

Hence it follows, that the vitriolic acid contains more specific fire, or at least gives out more on uniting to fixed alkalies, than either the nitrous or marine; and, therefore, when the vitriolic acid comes in contact with either nitre or salt of sylvius, its fire passes into these acids, which are thereby rarefied to a great degree, and are thus expelled from their alkaline  
basis,

basis, which is then seized on by the vitriolic. This explanation is confirmed by the following experiments.

Into 400 grs. of spirit of vitriol, whose specific gravity was 1,362, I put 60 grs. of nitre. The thermometer fell from 68 to 60, and during this time the nitrous acid was not expelled, for I put in some filings of copper, and they were not in the least acted upon; but in five minutes after, they visibly effervesced, which shews that the nitrous acid began to be expelled.

Again, to 400 grs of oil of vitriol, whose specific gravity was 1,870, I put 60 grs. of nitre: the thermometer immediately rose from 68 to 105°, and the nitrous acid was expelled in the form of a visible fume. These experiments prove, first, that neutral salts are not decomposed, by mere solution, in an acid different from that which they possess. 2dly, That the nitrous acid, being converted into vapour, had imbibed a large quantity of fire. But as the vitriolic, in both these experiments, was in much larger quantity than was necessary to saturate the alkaline basis of the nitre, I put 60 grs. of nitre into 64 of the above spirit of vitriol, which contained the same quantity of real vitriolic acid as the 60 grs. of nitre did of the nitrous, and added 40 grs. of water, and also a few grains of filings of copper. In less than two hours the copper was acted upon, and consequently the nitrous acid was expelled.

Again to about 400 grs. of oil of vitriol, whose specific gravity was 1,870, I put 100 grs. of common salt; it immediately effervesced, and gave out the marine acid in the form of a white vapour. A thermometer held in the liquor rose but 4°; but when placed in the froth it rose to 10°, and fell again on being put into the liquor: whence it follows, that the vitriolic acid gave out its fire to the marine, and that this latter received

more



more than it could absorb even in the state of vapour, and hence communicated heat to the contiguous liquor.

From these experiments it is evident, that the nitrous and marine acids receive fire from the vitriolic, and are thrown into a vapourous state, or at least so much rarefied as to be expelled from their alkaline basis, notwithstanding that their affinity to that basis may be equally strong with that of the vitriolic.

I next proceeded to examine how tartar vitriolate and GLAUBER's salt are decomposed by the nitrous acid. Into 400 grs. of spirit of nitre, whose specific gravity was 1,355, and which contained about 105 grs. of real acid, I put 60 of pulverised tartar vitriolate. The thermometer, which stood at 68°, was not in the least affected by standing in this mixture, and there was scarce any sign of solution. To try whether the vitriolic acid was disengaged, I threw into the liquor a few grains of powdered regulus of antimony: in 24 hours the vitriolic acid was in part disengaged, for the regulus was acted upon, and the liquor became greenish. This semi-metal being soluble in a mixture of the vitriolic and nitrous acids, but in neither singly, however, a great part of the tartar vitriolate still remained undissolved. Afterwards I put the same quantity of tartar vitriolate into 400 grs. of spirit of nitre, whose specific gravity was 1,478; the thermometer rose from 67 to 79°, the tartar vitriolate was quickly dissolved, and the regulus of antimony shewed the vitriolic acid was disengaged.

Hence it follows, that in the last experiment the nitrous acid having the same affinity to the alkaline basis as the vitriolic, but giving out, during the solution, more fire than was necessary to perform the solution, the vitriolic receiving this fire was disengaged; for as it cannot unite to alkalis without giving out fire, so when it receives back that fire it must quit them. The  
reason

reason why the nitrous acid, which specifically contains less fire than the vitriolic, gives out so much, is, that its quantity in both these experiments is far greater than that of the vitriolic; it being in the first as 105 to 17; and in the second as 158 to 17.

For this reason, to 60 grs. of spirit of nitre, whose specific gravity was 1,355, I added 1000 grs. of water, and into this dilute acid I put 60 grs. of tartar vitriolate, which contained exactly the same quantity of acid as the 60 grs. of spirit of nitre. After eight days the tartar vitriolate was almost intirely dissolved, yet I could perceive no sign of its decomposition, and after evaporation no nitre was found. Hence I conclude, that the nitrous acid can never decompose tartar vitriolate without the assistance of heat, but when its quantity is so great that it contains considerably more fire, and by the act of solution is determined to give out this fire. The decomposition of GLAUBER's salt and vitriolic ammon. (neither of which, as Mr. BERGMAN observed, is ever total) may be explained in the same manner; whereas the vitriolic, ever so dilute, decomposes both nitre and nitrous ammoniac totally. Tartar vitriolate is also decomposed by the marine acid, though very slowly, for the same reason, and in the same circumstances, as it is decomposed by the nitrous acid, as appears by the following experiments. Into 400 grs. of spirit of salt, whose specific gravity was 1,210, I put 60 grs. of tartar vitriolate. The thermometer was not in the least affected, and the salt dissolved very slowly. To try whether the vitriolic acid was disengaged, I added some pulverised bismuth; in twelve hours part of the bismuth was dissolved, and could not be precipitated by the affusion of water, a sign that it was held in solution by the compound acid, which alone hath the property of preventing

preventing its precipitation by the affusion of water, as Mr. WENZEL has discovered. Here the quantity of marine acid was much greater than that of the vitriolic, and consequently it contained more fire; but this circumstance alone is not sufficient, it must besides be determined to give out that fire by the act of solution. This appears by the experiments of Mr. CORNETTE; for when he mixed half an ounce of tartar vitriolate, *previously dissolved* in water with two ounces of spirit of salt, the tartar vitriolate was not decomposed, *Memoirs, Paris, 1778, p. 49.*; for it being already dissolved, no cold or heat was generated by mixing it with the spirit of salt, and consequently the latter did not give out any fire. Mr. CORNETTE also observed, that GLAUBER's salt is easier decomposed by the marine acid than tartar vitriolate; this I have also experienced, and the reason is, first, because GLAUBER's salt is more easily soluble in spirit of salt than tartar vitriolate; and, secondly, because its alkaline basis takes up a greater quantity of the real marine acid than of the vitriolic, whereas the basis of tartar vitriolate takes up an equal quantity of both acids; consequently the marine gives out more fire in uniting to the basis of GLAUBER's salt than on uniting to that of tartar vitriolate.

Vitriolic ammoniac is also decomposed by the marine acid for the same reason; but in all these cases the quantity of the marine acid must much exceed that of the vitriolic, or no decomposition will take place. The decomposition of nitro-neutral salts by the marine acid depends on the same principles. Mr. CORNETTE found, that cubic nitre was more easily decomposed than prismatic nitre, and accordingly, during the solution of prismatic nitre, only 3° of cold were produced; but, during that of cubic nitre, the thermometer fell 6°, a sign that the spirit of salt gave out more fire in the latter case than

in the former, and its quantity must always be greater than that of the nitrous acid contained in the mineral alkaline basis, because this basis requires for its saturation more of the marine than of the nitrous acid, as we have already seen.

Yet the nitrous acid, in its turn, decomposes salt of sylvius and common salt, as Mr. MARGRAF has shewn; but it must always be in greater quantity than the marine, in order to contain a sufficient quantity of fire for that effect. To 400 grs. of colourless spirit of nitre, whose specific gravity was 1,478, I put 60 grs. of common salt, it quickly effervesced and grew red; yet the thermometer rose but 2°, a sign that the marine acid had absorbed the greater part of the fire which the nitrous had given out, and was thus expelled: besides, in this case, the superior affinity of the nitrous acid to the mineral basis hastened the decomposition; and hence the decomposition happens without solution, whereas the marine acid does not decompose cubic nitre until it has dissolved it, which is worthy of notice. This mutual expulsion of the nitrous and marine acids by each other is the true reason why aqua regia may be made, as well by adding nitre or nitrous ammoniac to spirit of salt, as by adding common salt or sal ammoniac to spirit of nitre, as Mr. CORNETTE has well remarked.

Selenite is decomposed neither by the nitrous nor by the marine acids, as Messrs. CHAPTAL and CORNETTE have observed. The reason is evident on the above principles; it is dissolved by neither without the assistance of heat, and then the solution is performed by a *foreign* heat, and not by that which these acids give out when they act without the assistance of heat.

Lastly, whenever a vitriolico-neutral salt, decomposed by either the nitrous or marine acid, is evaporated to a certain degree, the vitriolic expels these acids in its turn; for the free

part of the former acids being expelled by the heat of evaporation, the neutral salts begin to crystallize, and consequently give out heat ; but the vitriolic being then in greater proportion re-acts on these salts, restores their specific fire to their acid principle, and recombines with their alkaline basis, as already explained.

Hence, though allum is in reality decomposed by the nitrous and marine acids, yet when the solution of it in either of these acids is evaporated to a certain degree, the vitriolic acid, of which it contains a larger proportion than any other terrene salt, re-acts on the nitrous and marine allums, and expels their acids, as Mr. CHAPTAL has shewn.

In explaining these phenomena I have all along supposed the doctrine of Dr. BLACK to be well known, *viz.* that solids absorb heat during their solution. Both the heat and cold, produced in different solutions, seem to me to depend on the same principle. If the menstruum gives out only *so much* of its fire as the solvent can absorb, or *less*, then cold is produced ; but if it gives out *more* of its specific fire than the solvent can absorb, this surplus becomes sensible, and affects the thermometer by producing heat in proportion to its quantity.

*Of the affinity of the mineral acids to metallic substances.*

Having thus, in every instance, established the agreement betwixt the quantity of any alkaline or terrene basis, taken up at the point of saturation by a given weight of any of the three mineral acids, and the quantity of affinity which each of these acids bears to such basis, I naturally extended my views to metallic substances, to try whether this coincidence could be traced with regard to them also ; but the difficulties that occurred in this inquiry were so great, that the same degree of certainty must not be expected as in the foregoing part.

Metallic

Metallic substances, when freed from all foreign mixture, are obtained either in a reguline state, or in that of a calx. These calces, if formed by fire, are constantly combined with more or less of the ærial acid, which is very difficultly extracted from them, and very soon re-absorbed; and if formed by solution, they as constantly retain a portion of their solvent or precipitant, so that the precise weight of the really metallic part is difficultly ascertained. But though this should easily be effected, still they would for the most part be unfit for my purpose; because most of them, when much dephlogisticated, are insoluble in some or all the acids: hence I chose metals in their metallic state for the subject of my experiments. These consist of specifically different earths and phlogiston, and of this they must lose a part before they can be dissolved in acids; but, besides that which escapes in an ærial form, much more of it, though separated from the metallic earth, is yet retained in the solution by the compound of acid and calx. It is this calx, thus differently dephlogisticated by the different acids, whose proportion I endeavoured to ascertain.

The great difficulty that occurred in this inquiry was, that of finding the exact quantity of acid necessary to saturate the metallic substances; for all metallic solutions turn solution of litmus red, and consequently contain an excess of acid. And the reason is, because the salts, formed by a due proportion of metallic calx and acid, are nearly insoluble in liquids that do not contain a further quantity of acid; and in some cases this quantity, and even its *proportion to the aqueous part of the liquor*, must be very considerable, as in solutions of bismuth. Hence I in vain endeavoured, by caustic alkalies and lime-water, to deprive these solutions of this excess; for when deprived even of only part of it, many of the metals precipitated, and all

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would,

would, if deprived of the whole of it. On this account I was obliged to use different methods, of which I shall here give an instance. With regard to the solution of silver in the nitrous acid, as it could be had extremely saturated I began with it. 657 grs. of this solution contained, according to my calculation, and allowing for the quantity of acid carried off in the nitrous air, 31,38 grs. of real acid, and 100 grs. of silver. Of this solution I found that 9 grs. gave a visible *red tint* to as much of a dilute solution of litmus, as a quantity of spirit of nitre, which contained  $\frac{8}{10}$ ths of a grain of real acid, and therefore I judged these 9 grs. to contain an excess of acid, amounting to  $\frac{8}{10}$ ths of a grain; and if 9 grs. contain such an excess, then the whole solution must have contained an excess amounting to  $5\frac{8}{10}$ ths of a grain, deducting which from 31,38, we find the quantity of acid saturated by 100 grs. of silver to be 25,78 grs. In this manner I proceeded with most other metallic solutions. The vitriolic solutions of tin, wismuth, regulus of antimony, nickel, and regulus of arsenic, containing a large excess of acid, I saturated part of it with caustic volatile alkali before I tried them with the infusion of litmus, and I used the same expedient with the nitrous solution of iron, lead, tin, and regulus of antimony, and all the marine solutions. The proportion of vitriolic and marine acid taken up by lead, silver, and mercury, I determined by computing the quantity of real acid necessary to precipitate these metals from their solutions in the nitrous acid; and of all the determinations these appeared to me to be the most exact. However, as all the vitriols of these metals are, though in a slight degree, soluble in the nitrous acid, I was obliged to rectify the result from other considerations, and the same necessity occurred with regard to the marine salts of lead and mercury.

The

The result of these experiments was, that 100 grs. of each of these acids take up, at the point of saturation of each metallic substance, dephlogisticated to such a degree as is necessary for its solution in each acid, the quantities expressed in the following table, which denote their degree of affinity to each metal.

*Table of the affinity of the three mineral acids to metallic substances.*

100 grs.	Iron.	Copper.	Tin.	Lead.	Silver	Mercury.	Zinc.	Wismuth.	Nickel	Cobalt.	Reg. of antimo.	Reg. of arsenic.
Vitriolic acid	270	260	138	412	390	432	318	$\frac{250}{310}$	320	360	200	260
Nitrous acid	255	255	120	365	375	416	304	290	300	350	194	220
Marine acid	265	265	130	400	420	438	312	$\frac{250}{320}$	$\frac{275}{310}$	370	198	290

Yet I cannot say that these numbers are *precisely* such as I could extract from my observations on the colour of the solution of litmus; for these indications are so precarious that I did not absolutely confide in them, but adjusted the numbers, as I thought other phenomena required. However, the deviations were not so considerable as to induce a doubt that metallic earths had not almost all a stronger affinity to the three acids than even fixed alkalies. Nevertheless, the common tables, which postpone metallic substances to all others, are in reality just; they only require a different denomination, being in fact tables of *precipitation* rather than of *affinity*, as far as they relate to metallic substances, expressing by their *order*, what metallic substances precipitate others from the different acids. But these precipitations are constantly the result of a double affinity and decomposition.



decomposition, the *precipitating* metal yielding its phlogiston to the *precipitated* metal, while the *precipitated* metal yields its acid to the *precipitant*. Nor has this escaped the sagacity of Mr. BERGMAN, 2 N. Act. Upf. 205, who has even confirmed it by experiments which I have repeated, and found exact. Thus, though copper, in its metallic form, precipitates silver and mercury from the nitrous acid with great ease, yet the calx of copper will precipitate neither. The superior affinity of acids to metallic earths, in preference to alkalies and unmetallic earths, requiring further proof, I shall here demonstrate it in a few instances, with regard even to those metals which are commonly thought to have the least affinity to acids. And, first, that the nitrous acid has a stronger affinity to silver than to fixed alkalies, appears by a curious experiment of Mr. MONNET's (*Dissolution des Metaux*, p. 159.). If a solution of silver in nitrous acid be poured into a mixed solution of fixed alkali and common salt, the silver will be precipitated by the marine acid of the common salt, and not by the free alkali contained in the liquor, for a *luna cornua* is found. Now if the nitrous acid had a greater affinity to the free alkali than to the silver, it is evident, that the decomposition would be wrought by the free alkali, and then the silver would be precipitated pure, and not in the state of horn silver; but as it is precipitated in the state of horn silver, it is plain, its precipitation was not effected by a single but by a double affinity. From whence it also follows, that the marine acid has a greater affinity to silver than the nitrous has to fixed alkalies. I repeated this experiment with a solution of lead and also of mercury in the nitrous acid, and the result was similar, horn lead and marine salt of mercury being formed.

With

With regard to mercury, the experiments of Mr. BAYEN are well known: he has shewn that vitriol of lead and sub. corrosive can be deprived of no more than half of their acid even by caustic fixed alkalies, 3 ROZ. 293.

Again as to lead, if perfectly dry common salt be projected on lead heated to incandescence, the common salt will be decomposed, and horn lead formed, 1 MARGRAF. 35 and 38. Nor can this be attributed to the volatilization of the acid by heat; for the alkali is as fixed as the lead, and must therefore be caused by the greater affinity of the calx of lead, to which, when dephlogisticated, the acid can unite. Mr. SCHEELÉ informs us, that if a solution of common salt be digested with litharge, the common salt will be decomposed, and a caustic alkali produced, SCHEELÉ on Fire, p. 175. He also decomposes common salt by simply letting its solution slowly pass through a funnel filled with powdered litharge. \* Mr. TURNER daily decomposes common salt by means of litharge. Mr. SCHEELÉ also decomposes marine selenite, by means of litharge, through simple mixture, without the assistance of heat, and the calcareous earth is separated in a caustic state; which shews that this salt is decomposed by the single superior affinity of the metallic calx to the marine acid, SCHEELÉ on Fire, p. 174.

That acids have less affinity to volatile alkalies than to several metallic substances appears in sundry instances. Horn silver is soluble in volatile alkalies, as is well known. Now, if this solution be triturated with four times its weight of mercury, the marine acid will combine with the mercury, and not with the volatile alkali; for a *mercurius dulcis*, and not a sal ammoniac, will be formed, as Mr. MARGRAF has shewn, 1 MARG. 286. If two parts sal ammoniac and one of filings of iron be

\* SCHEFFER Chymische Focceles, § 59.

trituated together, the smell of the volatile alkali will immediately be perceived \*; or if, instead of iron, minium, or diaphoretic antimony, or zinc, be used, that smell is perceived as soon as they are mixed, 9 Mem. Scav. Etrang. p. 575. MONNET, Diss. Met. 209. But it will naturally be asked, how then it happens, that all metallic solutions are precipitated by alkalies and earths? The answer is easy; all metallic salts are held in solution by an excess of acid. If alkalies and earths did nothing more than absorb this excess of acid, a precipitation ought to take place; but they do still more, for they take up the greater part even of the proportion of acid necessary to saturate the metallic earth, and this they are enabled to do by means of a double affinity; for during the solution of metals, only a comparatively small part of the phlogiston escapes out of the solution, the remainder is retained by the compound of acid and calx: when, therefore, an alkali or earth is added to such a solution, the phlogiston quits the acid, and re-combines with the calx, while the greater part of the acid unites to the precipitant. Notwithstanding this great affinity of metallic earths to acids, salts, whose basis is a fixed alkali or earth, are in few instances decomposed by metals or their calces, by reason of the inability of the acids while combined with these basis, and thereby deprived of a great part of their specific fire, to volatilize the phlogiston combined with the metallic earths, which must necessarily be expelled before an acid can combine with them. And as to metallic calces, they are generally combined with fixed air, which also must be in part expelled.

But ammoniacal salts, containing much more fire (for they absorb fire during their formation) for that reason act much more powerfully on metals. Allowing then the affinity of the

\* MONNET, Dissol. Met. 71.

mineral acids to metallic substances to be as above, all double decomposition in which only salts, containing these acids united to alkaline terrene or metallic bases, are concerned, admit of an easy explanation; nay, I am bold to say, they cannot otherwise be explained. Thus if a solution of tartar vitriolate, and of silver in the nitrous acid, be mixed in proper proportions (which is always to be understood), nitre and vitriol of silver will be formed, and this latter for the most part precipitated.

Quiescent affinities.			Divellent affinities.	
Nitrous acid to silver	-	375	Nitrous acid to vegetable alkali	215
Vitriolic acid to vegetable alkali		215	Vitriolic acid to silver	390
Sum of the quiescent	-	590	Sum of the divellent powers	605

So also if, instead of a solution of tartar vitriolate, that of GLAUBER'S salt, or of vitriolic-ammoniac, or selenite, Epsom, or allum, be used; for in all these cases the balance is constantly in favour of the divellent powers, yet the solutions of selenite and allum produce but a slight precipitation.

I also found, that the solution of silver is precipitated by the vitriolic solutions of iron, copper, tin, and probably by many other vitriolic solutions, if for no other reason at least for this, that they constantly contain an excess of acid; but if a saturate solution of silver be mixed with a very saturate solution of lead or mercury in the vitriolic acid, the silver will not be precipitated, as I have observed; and in both cases the balance is in favour of the quiescent affinities.

The nitrous solution of silver is also decomposed, and the silver precipitated by all *marino* neutral salts, whether the basis be alkaline, terrene, or metallic, as I have experienced, and

these decompositions are constantly indicated by the balance of affinities exhibited as above.

In the same manner silver is precipitated from the *vitriolic* acid by *marino* neutral salts, whether their basis be alkaline, terrene, or metallic, as I have found on trial, and as the balance of affinities requires.

The nitrous solution of lead is also decomposed, and the lead for the most part precipitated (unless the solution be very dilute) in the form of vitriol of lead by all the *vitriolico* neutral salts; and also by all the *marino* neutral salts, except marine salt of silver, which only precipitates it by virtue of its excess of acid.

The marine solution of lead is decomposed by all *vitriolico* neutral salts, except selenite and vitriol of nickel, which can only precipitate it by virtue of an excess of acid.

The nitrous solution of mercury is also decomposed, and the mercury for the most precipitated in the form of vitriol of mercury by all vitriolic neutral salts, except vitriol of lead, which can only decompose it by an excess of acid.

Nitrous solution of mercury is also decomposed by *marino* neutral salts, except the marine salt of silver and lead, which can only affect it by an excess of acid.

Vitriol of mercury is also decomposed by *marino* neutral salts, which decomposition is also apparent by exposing the antagonist powers; yet a precipitation does not always appear as I have remarked, particularly when marine allum is used, which I attribute to the facility with which a small quantity of the marine salt of mercury is soluble in an excess of acid. Marine salt of silver decomposes vitriol of mercury, only through its excess of acid.

Hence we see why horn silver can never be reduced by fixed alkalies without loss, as Mr. MARGRAAF has shewn, I MARGR. 277.; nor could it be decomposed at all, but that the action of heat helps that of the alkali.

If to a solution of sublimate corrosive oil of vitriol be added, a precipitation will appear; but, as Mr. BERGMAN well remarks, this does not proceed from a decomposition, but from a subtraction of the water necessary to keep the sublimate dissolved.

If to a solution of vitriol of iron some nitrous acid be added, it immediately becomes turbid, because the nitrous acid dephlogisticates the calx of iron too much, but the addition of more acid restores the transparency, as the dephlogisticated calx is still soluble by a greater quantity of acid. I omit a number of other curious phenomena, which are explicable on these principles.

I have assigned in the foregoing table two different affinities to the vitriolic acid with regard to wismuth, and also to the marine acid with regard to nickel and wismuth. The first shews that which these acids bear to those metals, when dephlogisticated only by solution in those acids. The second number, that which the acids bear to them when more dephlogisticated, as they are, when dissolved in the nitrous acid. On the other hand, all the acids have less affinity to the calces of iron, zinc, tin, and antimony, when they are dephlogisticated to a certain degree; but as I could give no criterion of this dephlogistication, I did not attempt to indicate the diminution it causes in the affinities of acids.

*Of the precipitation of metals by each other from the mineral acids.*

I am now come to the last point of my inquiry, and the most difficult to be set forth with that degree of precision which I have been enabled to attain in the former parts; for, in the first place, it is necessary to find the quantity of phlogiston in each of them, not only in general, but according to their various degrees of dephlogistication by each of the acids. In this last particular I cannot assert that I have attained any thing like a certainty, yet I hope what I advance may not be useless to chymical readers, as it is not altogether groundless, as it contradicts no chymical fact, but, on the contrary, is agreeable to many, and affords a ready solution of all the phenomena.

*Of the absolute quantity of phlogiston in metals.*

The proportion of phlogiston in metallic substances relatively to each other has been investigated in so masterly a manner by Mr. BERGMAN, that I lay it down as the ground of my inquiries. After his discovery all that remained was to find the absolute quantity of it in any one metal, for then, by an easy calculation, it may be determined in all the rest. The substance I chose for this purpose was regulus of arsenic, as being most capable of dephlogistication by nitrous acid, though not altogether so.<sup>1</sup>

From 100 grs. of regulus of arsenic, dissolved in dilute nitrous acid, as already seen, 102 cubic inches of nitrous air and  $\frac{4}{7}$ ths are obtained, barometer at 30°, thermometer at 60°. I must add, that I made the experiment on 5 grs. only, so that the calculation relates only to the quantity of air which 100

grs.

grs. *should* give. I repeated the experiment three times with the same success. I attempted getting more air from the residuum left by a gentle evaporation, but though fresh spirit of nitre grew red with it, the quantity of air was quite inconsiderable.

Now this quantity of nitrous air contains 6,86 grs. of phlogiston, according to the calculation to be seen in my former paper; and hence I conclude, that 100 grs. of regulus of arsenic contains 6,86 grs. of phlogiston. This regulus was made by Mr. WOLFE, and perfectly bright.

Hence the relative proportion of phlogiston in metals being, as found by Mr. BERGMAN, and set forth in the first column of the following table, the absolute quantity will be as shewn in the second column.

	Relative quantity of phlogiston.				Absolute quantity.	
100 grs. Gold	-	-	394	-	-	24,82
Copper	-	-	312	-	-	19,65
Cobalt	-	-	270	-	-	17,01
Iron	-	-	233	-	-	14,67
Zinc	-	-	182	-	-	11,46
Nickel	-	-	156	-	-	9,82
Regulus of antimony	-	-	120	-	-	7,56
Tin	-	-	114	-	-	7,18
Regulus of arsenic	-	-	109	-	-	6,86
Silver	-	-	100	-	-	6,30
Mercury	-	-	74	-	-	4,56
Wismuth	-	-	57	-	-	3,59
Lead	-	-	43	-	-	2,70

This point being, as I conceived, of some importance, I endeavoured to ascertain it still further by other experiments: and



as silver loses a certain quantity of phlogiston, which escapes and separates from it during its solution in nitrous acid, I conceived, that if the solution was exposed to nothing from which it could re-obtain phlogiston, and thus distilled to dryness, and entirely separated from the acid, as much silver should remain unreduced as corresponded with the quantity of phlogiston lost by it. And if this quantity of phlogiston corresponded with that assigned to silver in the foregoing table, that then this table was just.

For this purpose I dissolved 120 grs. of clean filings of standard silver in dilute dephlogisticated nitrous acid, and obtained from it 24 cubic inches of nitrous air. This solution I gently evaporated to dryness; by the evaporation I found a little of the silver volatilized, but not more than a quarter of a grain. I then distilled the dry residuum, and kept it an hour in almost a white heat in a coated green glass retort. During the distillation abundance of the nitrous acid passed off, a green and white sublimate arose in the neck of the retort, and some passed even into the receiver. When all was cold I broke the retort, the inside of which was penetrated into its very substance with a yellow and red tinge, and partly covered over with an exceeding fine silver powder, which could scarcely be scraped off. The remainder of the silver was perfectly white and free from acid, but not melted into a button, and when collected weighed 94 grs.; therefore 26 grs. were lost, that is, were sublimed or vitrified; but of these 26 grs. 9 grs. were copper (for 100 grs. standard silver contain  $7\frac{1}{2}$  of copper); therefore, only 17 grs. of pure silver remained unreduced, being either volatilized or vitrified. The whole quantity of pure silver in 120 grs. of standard silver amounts to 111 grs.; then if 111 grs. of pure silver lose 17 by reason of its  
loss

loss of phlogiston, 100 grs. of pure silver should lose 15,3; and by the above table 15,3 grs. of silver should contain 0,945 of a grain of phlogiston. Let us now see whether this quantity of phlogiston corresponds with that which 100 grs. of pure silver really lose by solution in nitrous acid. 100 grs. of pure silver afford, as already said, 14 cubic inches of nitrous air, which, by my computation, contain 0,938 of a grain of phlogiston, which differs from 0,945 only by  $\frac{7}{1000}$ . The unreduced part of the silver was 15,3 grs.; and, by calculating what it should be by reason of the loss of the phlogiston contained in the nitrous air, it would amount to 14 and  $\frac{2}{10}$ ths of a grain, a difference certainly immaterial.

In this experiment, only as much of the silver sublimed as could not regain phlogiston; the remainder regained it from the nitrous air absorbed by the solution, and also from that which remained united to the acid and calx. If this were not so, I do not see why the whole of the silver would not sublime.

Again: Dr. PRIESTLEY having several times dissolved mercury in the nitrous acid, and revived it by distilling over that acid, constantly found a considerable proportion of it unreduced. To try whether that proportion corresponded with my calculation, I have examined the experiment which he made with most care, and which is to be found in his 4th vol. p. 262. We there find, that having dissolved 17 dwts 13 grs. = 321 grs. of mercury in nitrous acid,  $1\frac{1}{2}$  dwt. that is, 36 grs. remained unreduced. Now, according to my calculation, 56 grs. should remain unreduced; for 100 grs. of mercury afford 12 cubic inches of nitrous air; therefore 321 grs. should afford 38,52, which contain 2,58 grs. of phlogiston, and if (according to the table) 4,56 grs. of phlogiston be necessary to metallize 100 grs. of mercury, 2,58 will be necessary to metallize 56 grs.

of mercury : and I am satisfied, from my own trials, that more than 50 grs. would be found unreduced if dephlogisticated nitrous acid had been used in dissolving the mercury, and the solution performed with heat and a strong acid ; but that which Dr. PRIESTLEY used, being the red or yellow sort, already contained much phlogiston, which contributed to the revivification of a larger quantity of mercury than would otherwise be found. It is true, that Dr. PRIESTLEY afterwards revived a great part of what originally remained unreduced ; but this happened after it was for some time exposed to the free air, from which the calces of the perfect metals always attract phlogiston, as is evident in luna cornua, which blackens on exposure to the air, and hence also proceed the reductions operated by Mr. BAYEN.

But Dr. PRIESTLEY, to whose luminous experiments chymistry is already so much indebted, has been so obliging as to furnish me with some which tend more directly to elucidate the present question.

In one experiment he found that nearly 5 dwts. of minium, from whence all its air was extracted, that is, about 118 grs. absorbed 40 oz. measures of inflammable, that is, 75,8 cubic inches = 2,65 grs. of phlogiston, and were then reduced : then 100 grs. of minium should require for their reduction nearly 2,25 grs. of phlogiston. In another experiment, made with more care, he found, that 480 grs. of minium absorbed 108 oz. measures of inflammable air ; according to this then 100 grs. of minium require for their reduction 1,49 grs. of phlogiston ; and in two other experiments he found this quantity still less. Upon which I remark, first, that the whole of the minium was not dephlogisticated ; for, besides that it is never throughout equally calcined, much of it must have been reduced

reduced during the expulsion of its air; secondly, that the quantity of the phlogiston in the inflammable air may have been greater as this varies with its temperature, and the weight of the atmosphere; so that upon the whole these experiments confirm the results expressed in the table.

*Of the affinity of metallic calces to phlogiston.*

That inflammable air or phlogiston is condensed to a very considerable degree by uniting to any metallic substance, so that its specific gravity is not only equal, but much superior, to that of the metallic earth with which it combines, may easily be concluded from the example of fixed air, which, by uniting to calcareous earth, acquires a specific gravity equal to that of gold; and hence, that metallic earth which condenses phlogiston most, and in greatest quantity, uniting to it most closely, may be said to have the greatest affinity to it; so that if we could find the specific gravity of a calx perfectly pure, both from phlogiston and fixed air, we could, by comparing its density with that of the same calx when metallized, know the density which phlogiston acquires by its union with such calx; but to procure such calces hath hitherto proved impossible, as, during their dephlogistification, they combine with fixed air, or some particles of their menstruum; and hence their absolute weight is increased, though their specific gravity be somewhat diminished. From this last circumstance it appears, that the specific gravity of calces differs much less from that of their respective metals than does the specific gravity which the phlogiston acquires by its union with those calces, from that which it possesses in its uncombined state; in the same manner as the density of quick-lime differs much less from that of limestone, than does the density which fixed air acquires by its

union with quick-lime from that which belongs to it in its aërial state; and hence, instead of deducing the quantity of affinity of metallic calces to phlogiston from the following proposition, *viz.* that *the affinity of metallic calces to phlogiston is in a compound ratio of its quantity and density in each metal*, I am obliged to deduce it from this other, *viz.* that *the affinity of metallic calces to phlogiston is directly as the specific gravity of the respective metals, and inversely as the quantity of calx contained in a given weight of those metals*. This latter proposition is an approximation to the former, founded on this truth, that *the larger the quantity of phlogiston in any metal is, the smaller is the quantity of calx in a given weight of that metal*; and that *the density which the phlogiston acquires, is as the specific gravity of the metal*. This latter proposition, however, is not exactly true, for this density is much greater; yet it is the nearest approximation I can make, and its defect is sensible only with regard to those metals which contain a considerable quantity of phlogiston, *viz.* gold, copper, cobalt, and iron: with regard to the rest it is of no importance.

Then the specific gravity of metals being as represented in the first column of the following table, the affinity of their calces to phlogiston will be as is shewn in the second column. The third column expresses these affinities in numbers homogenous with those which express the affinities of acids with their basis.

Specific gravity.				Affinity of the calces to phlogiston.	
Gold	-	19	-	0,25	1041
Mercury	-	14	-	0,147	612
Silver	-	11,091	-	0,118	491
Lead	-	11,33	-	0,116	483
Copper	-	8,8	-	0,109	454
Wismuth	-	9,6	-	0,099	412
Cobalt	-	7,7	-	0,092	383
Iron	-	7,7	-	0,090	375
Regulus of arsenic	-	8,31	-	0,089	370
Zinc	-	7,24	-	0,0817	340
Nickel	-	7,33	-	0,0812	338
Tin	-	7,	-	0,075	312
Regulus of antimony	-	6,86	-	0,074	308

Here we see, that the calx of lead has a greater affinity to phlogiston than the calces of any of the imperfect metals, and hence its use in cuppellation; for after it has lost its own phlogiston, it extracts that of the base metals, and thus promotes their calcination and vitrification.

Though the numbers in the second column express tolerably well the greater or lesser affinity of metallic calces to phlogiston, yet they have this inconvenience, that they are not homogenous with those that express the affinities of acids to other bases, which limits their use to a narrow compass, they being, on that account, incomparable with those that express the affinities of acids: I therefore endeavoured to find a coincidence between them in some one instance, in order to reduce them to the same standard, as will be seen in the next paragraph.

*Of the affinity of the vitriolic acid to phlogiston in sulphur.*

According to the principle above laid down, this affinity is in a compound ratio of the quantity of phlogiston taken up by 100 grs. of the vitriolic acid and of the density it acquires by its union with the acid. Now 100 grs. of sulphur contain 59 of acid and 41 of phlogiston, and the specific gravity of sulphur is 2,344; therefore, the loss of weight of sulphur in water =  $\frac{100}{2,344} = 42,66$  grs. the loss of weight of the acid part of the sulphur is  $\frac{59}{2,226} = 13,96$  grs.; therefore, the remainder of the loss of sulphur is the loss of the phlogistic part = 28,70 grs.; then the absolute weight of the phlogiston being 41 grs. its density will be  $1,429 = \frac{41}{28,7}$ ; and since 100 grs. of vitriolic acid take up 70 of phlogiston its affinity will be  $1,429 \times 70 = 100$ . But if the affinity of the vitriolic acid to phlogiston in sulphur had been sought in the same manner with the affinity of metallic calces to phlogiston, the quantity would be the same, though the expression of that quantity would be different, as relating to a different standard; for by that method the affinity would be directly as the density of the phlogiston, and inversely as the quantity of vitriolic acid contained in 100 grs. of sulphur, that is,  $\frac{1,429}{59} = ,024$ ; therefore, this expression answers to, and is equivalent to the former, *viz.* 100. By this means I formed the quantities expressed in the third column, which are homogenous to those which express the affinities of acids to their basis. Thus, the affinity of the calx of gold to phlogiston is 1041, for  $::,024 \cdot 100 :: ,25 \cdot 1041$ , &c.

The

The third point necessary for the explanation of the phenomena attending the solution of metals, and their precipitation by each other, is to determine the proportion of phlogiston which they lose by solution in each of the acids, and the affinity which their calces bear to the part so lost. I have not been able to determine this by any direct experiment; for though I might determine the part which escapes in the form of air, yet I could not that which is equally separated from the metal, but retained in the solution; yet from various collateral considerations I am induced to think, the proportion of phlogiston, separated from the metals by the different acids, is, at a medium, as expressed in the following table.

	Iron.	Copper.	Tin.	Lead.	Silver.	Mercury.	Zinc.	Wit-muth.	Cobalt.	Nickel.	Reg. of antime.	Reg. of arsenic.
By vitriolic acid	$\frac{2}{3}$	$\frac{8}{10}$	$\frac{7}{10}$	$\frac{98}{100}$	Intire	$\frac{87}{100}$	$\frac{85}{100}$	$\frac{85}{100}$	$\frac{93}{100}$	Intire	$\frac{97}{100}$	$\frac{86}{100}$
By nitrous acid	$\frac{2}{3}$	$\frac{81}{100}$	$\frac{7}{10}$	$\frac{88}{100}$	Intire	$\frac{9}{10}$	$\frac{99}{100}$	$\frac{97}{100}$	Intire	Intire	Intire	$\frac{99}{100}$
By marine acid	$\frac{42}{100}$	$\frac{57}{100}$	$\frac{3}{10}$	$\frac{6}{10}$			$\frac{6}{10}$	$\frac{7}{10}$	$\frac{94}{100}$	$\frac{8}{10}$	$\frac{84}{100}$	$\frac{8}{10}$

On this supposition the affinity of the calces to the deficient part of their phlogiston may easily be calculated; for they may be considered as acids whose affinity to the deficient part of their basis is as the ratio which that part bears to the whole, as already said. Thus the affinity of iron, thoroughly deprived of its phlogiston, being 375, as it loses  $\frac{2}{3}$ ds of its phlogiston by solution in the vitriolic acid, the affinity of iron to these two-thirds is  $\frac{2}{3}$ ds of its whole affinity, that is,  $\frac{2}{3}$ ds of  $375 = 250$ .

These affinities, together with those of the three acids to the several calces, are represented together in the following table.

Vitriolic



	Iron.	Copper.	Tin.	Lead.	Silver	Mercury.	Zinc.	Wismuth.	Cobalt.	Nickel.	Reg. of antimo.	Reg. of arsenic.
Vitriolic acid	270	260	138	412	390	432	318	250.310	360	320	200	260
Calx to phlog.	250	360	218	483	491	532	298	350	300	338	300	320
Nitrous acid	255	255	120	363	375	416	304	290	350	300	194	255
Calx to phlog.	250	363	218	424	491	552	337	400	383	338	308	366
Marine acid	265	205	130	400	420	438	312	250.320	370	275.310	198	290
Calx to phlog.	165	260	104	290	491	500	200	280	360	265	240	300

The affinities of calces to phlogiston are taken at a medium ; for almost all metallic substances are capable of greater or lesser dephlogistication, according to the species, concentration, and dephlogistication of their menstruum. The more they are dephlogisticated, the greater their affinity to phlogiston ; and, in general, the less their affinity to the mineral acids. Yet there is a point of dephlogistication at which the attraction of acids to the calces is strongest : thus the vitriolic acid attracts bismuth most strongly after it has been dephlogisticated by the nitrous acid ; and the marine acid attracts both bismuth and nickel more powerfully, when dephlogisticated by the nitrous or vitriolic acids.

From these *data* we may easily conceive, in most cases, what will happen on putting one metal into the solution of another.

Thus, if a piece of copper be put into a saturated solution of silver, the silver will be precipitated ; for the balance is in favour of the divellent powers.

Quiescent affinities.		Divellent affinities.	
Nitrous acid to silver	375	Nitrous acid to copper	255
Calx of copper to phlogiston	363	Calx of silver to phlogiston	491
Sum of the quiescent affinities	738	Sum of the divellent	746

The solutions must be nearly saturate, else a large quantity of the added metal will be dissolved by the free acid, before any precipitation can appear; yet it must not be intirely saturate, at least in some cases, as will presently be seen.

I said in *most cases*, because in some, particularly where mercury, bismuth, cobalt, regulus of antimony or arsenic, are used, another power intervenes which has not yet been fully investigated, *viz.* the attraction of calces to each other, which I shall occasionally mention.

It is worthy of observation, that the precipitating metals are more dephlogisticated by this means than by direct solution in their respective menstrooms, and are even dissolved by menstrooms that would not otherwise affect them; because their phlogiston is torn from them by two powers instead of one: thus, though copper be directly soluble in the vitriolic acid, only when this acid is concentrated and heated to a great degree, yet if a piece of copper be put into a dilute cold solution of silver or mercury in the vitriolic of acid, or even into a dilute solution of iron, exposed to the open air, it will be dissolved; a circumstance which justly excited the wonder of Mr. MARGRAAF and Mr. WENZEL, who did not apprehend the theory of it: and hence we see how vitriol of copper may be formed by nature, and why it always contains a mixture of iron.

#### *Of solutions in the vitriolic acid.*

This acid dissolves iron and zinc, without the assistance of heat; because its affinity to their calces is greater than the affi-

nity

nity which these calces bear to that portion of phlogiston which they must lose before they can unite to the acid, as may be seen by inspecting the table; but all other metallic substances unite to this acid only where it is concentrated and heated.

*Of solutions in the nitrous acid.*

The nitrous acid has less affinity to all metallic substances than either the vitriolic or marine. It has also less affinity to them than they have to that portion of phlogiston which they must lose before they can unite to it; yet it dissolves them all (gold and platina excepted) even without the aid of heat because it unites itself to phlogiston unless too dilute; and the heat produced by its union with phlogiston is sufficient to promote the solution.

But if it be too concentrated, it will not act either on lead or silver, without the assistance of heat, as BOYLE and BOERHAAVE have remarked\*; for the difference betwixt its affinity to these metals, and that of these metals to the portion of phlogiston which they must lose before they can unite to it, is very great; and when it is very concentrated, the liquor does not contain fire enough to throw the phlogiston and it into an aerial form, and reduce the solid to a liquid; the same would probably be observed with regard to mercury, if it had not been already in a liquid state. STAHL has also remarked, that it produces very little heat in dissolving silver, and none in dissolving lead or mercury†. This is easily explained, now that we know that silver contains but little phlogiston, and lead much less, the heat being evidently produced, according to the

\* I SHAW'S BOERH. 508. 2 SHAW'S BOYLE 335.

† STAHL sur les sels 168.

law discovered by Dr. CRAWFORD, by the union of phlogiston to the acid, for metallic calces produce no heat. As to mercury, the observation is not exact, for its solution is accompanied with heat, as Mr. LAVOISIER has observed, 1 LAVOIS. 248.

*Of solutions in the marine acid.*

This acid is known to dephlogisticate metals less than any other. Where the portion of phlogiston, necessary to be separated, is more strongly attracted than the acid itself, it can operate no solution, or at least very slowly, without the aid of heat; nor even where the attraction of acid is stronger to the calx than that of the portion of phlogiston it separates, if the proportion of acid to such calx be very small; because so small a quantity of acid does not contain fire enough to volatilize the phlogiston; and hence heat is necessary for the solution of lead in this acid. The dephlogisticated acid acts more powerfully.

*Of precipitations of and by iron.*

The mutual precipitations of iron and copper from the vitriolic acid by each other, have been well explained in a general manner by Mr. MONNET and Mr. BERGMAN; I shall here shew the reason of these precipitations more distinctly.

If a piece of copper be put into a saturate solution of iron, fresh made, no precipitation will happen, nor will any of the copper be dissolved in twelve hours, nor even in a longer time, if the access of air to the solution be prevented; but if the solution be exposed to the open air, the addition of a volatile alkali will shew the copper to have been acted upon in 24 hours, or sooner if heat be applied, and a calx of iron is precipitated. The operation of the affinities in the first case is as follows.

Quiescent.		Divellent.	
Vitriolic acid to calx of iron	270	Vitriolic acid to copper	260
Copper to its phlogiston -	360	Calx of iron to phlogiston	250
Sum	630	Sum	510

Hence, in this case, no decomposition can happen; but in the second case, much of the phlogiston of the solution of iron having escaped, the affinity of the calx of iron to acid is diminished, and that to phlogiston is increased, and therefore the quiescent affinities may be supposed,

		and the divellent.	
Vitriolic acid to the calx of iron	240	Vitriolic acid to copper -	260
Copper to its phlogiston -	360	Calx of iron to phlogiston	370
	600		630

But from the increased affinity of the calx of iron to phlogiston it might be inferred, that as the iron recovers its phlogiston, the acid should re-act upon it and quit the copper; and this would certainly happen, if it recovered its phlogiston in sufficient quantity, but the access of air and heat prevents its retaining it, at least in sufficient quantity.

This increased affinity of the calx of iron to phlogiston is not a mere supposition; for, if into a solution of iron, so far dephlogisticated as to refuse to crystallize, some fresh iron be put, the impoverished calx will re-attract so much of the phlogiston given out during the solution of the fresh iron, that it will now afford crystals, as Mr. MONNET has observed in his excellent Treatise on Vitriolization. The diminished attraction of the calx of iron to acids is also evident from this experiment,

and also from the necessity of adding more acid to a turbid solution of iron, in order to re-establish its transparency. The calces of copper also precipitate a dephlogisticated solution of iron, as they should, the affinity of the acid to such calx of iron being 240, and that to copper being 260. With regard to the solution of iron in nitrous acid, the same thing happens; but as this solution contains a large excess of acid, a portion of copper is dissolved even before any of the iron is precipitated.

With regard to a solution of iron in the marine acid, though exposed to the open air, copper precipitates nothing from it in 24 hours.

But if a clean piece of iron be put into a solution of copper in the vitriolic acid, the copper is immediately precipitated; for here the quiescent and divellent affinities exhibited in the first scheme are reversed, the quiescent becoming the divellent, and *vice versa*. It is needless to add, that copper is in the same manner precipitated by iron from the nitrous and marine acids.

Hence the practice of extracting copper from some mineral waters by means of iron. These waters, therefore, furnish afterwards, by evaporation, vitriol of iron; but it is remarkable, that this vitriol is much paler than the common, and less fit for dying, 2 SCHLUTTER 507. The reason of which is, that it is more dephlogisticated, not only because old iron is chiefly used, but because copper, containing more phlogiston than an equal weight of iron, deprives it of more of its phlogiston than it would lose if barely dissolved in the vitriolic acid.

Cast iron, according to SCHLUTTER, will scarcely precipitate a solution of copper; and in effect Mr. BERGMAN has found that it contains less phlogiston than bar iron.

I have always found silver to be easily precipitated from its solution in the nitrous acid by iron. The sum of the quiescent affinities being 625, and that of the divellent 746; yet Mr. BERGMAN observed, that a very saturated solution of silver was very difficultly precipitated, and only by some sorts of iron, even though the solution was diluted, and an excess of acid added to it\*; the reason of this curious phenomenon appears to me deducible from a circumstance first observed by Mr. SCHEELÉ, in dissolving mercury, namely, that the nitrous acid, when saturated with it, will take up more of it in its metallic form†. The same thing happens in dissolving silver in the nitrous acid in a strong heat; for, as I before remarked, the last portions of silver thrown in afford no air, and consequently are not dephlogisticated. Now this compound of calx of silver, and silver in its metallic form, may well be unprecipitable by iron, the silver, in its metallic form, preventing the calx from coming in contact with the iron, and extracting phlogiston from it: and hence also, iron has sometimes been observed not to precipitate a solution of mercury in this acid‡.

It has been long thought, that iron may be precipitated from acids by zinc, though NEWMAN long ago denied it; but Mr. BERGMAN has satisfactorily cleared up this point, by shewing that zinc cannot precipitate iron from the vitriolic acid, until the solution of iron loses part of its phlogiston. With regard to the nitrous acid, I found, that zinc does not precipitate iron; but, on the contrary, iron precipitates zinc; but in a short time the acid re-dissolves the zinc, and lets fall the iron, which evidently proceeds from the too great dephlogistication of the calx of iron. But zinc precipitates iron from the marine,

\* Dissert. de Phlog. Quantitate in Metal. p. 6.

† 39 SUENSK. Handling, p. 70.

‡ 2 CRELL. Nev. Entdeck. p. 266.

though with difficulty; for after 24 hours the galls still struck a black. I should also add, that iron does not precipitate zinc from the vitriolic acid.

Most metallic substances, precipitated by iron from the nitrous acid, are in some measure re-dissolved shortly after, as the nitrous acid soon dephlogisticates the iron too much, then lets it fall, and re-acts on the other metals and re-dissolves them.

The precipitation of the argillaceous earth from allum by iron is owing to the excess of acid in the allum which first dephlogisticates the iron; and when this is dephlogisticated, it attracts the acid more strongly. Earth of allum, on the other hand, precipitates iron when the solution of iron is dephlogisticated by heat. It may also produce this effect by depriving iron of its excess of acid which keeps it in solution.

#### *Of precipitations of and by copper.*

When silver is dissolved in the nitrous acid, and a piece of copper is put into the solution, it sometimes happens, that the silver is not precipitated, as Dr. LEWIS has observed\*. This happens either when the nitrous acid is supersaturated with silver having taken up some in its metallic form, as already observed; or when the silver is not much dephlogisticated, for then its affinity to phlogiston, which is the principal cause of its precipitation, is less than 491; therefore, the remedy is to heat it and add more acid, by which it is dephlogisticated further. However, the nitrous acid always retains a little silver. SCHLUTTER. 362. Hist. Mem. Par. 1728.

It is commonly said, that if filings of copper be put into a boiling solution of allum, vitriol of copper will be found, and

\* *Commercium Philos.* p. 157.



the earth of allum precipitated. If this were true it would be very surprizing, as copper is soluble, even with the assistance of heat, only in the concentrated vitriolic acid. Hence I made the experiment, and found, that after 20 hours boiling not the smallest particle of copper was dissolved, for the colour of the solution was not altered by volatile alkalies : and though the allum was precipitated, it still retained its saline form, so that it lost only its excess of acid in this experiment.

*Of precipitations of and by tin.*

Tin is not precipitated, in its metallic form, by any metallic substance ; and the reason is, because its precipitation is not the effect of a double affinity, but of the single greater affinity of its menstruum to every other metallic earth. Metals that are precipitated from the nitrous acid by tin, are afterwards redissolved, because the acid soon quits the tin, it becoming too much dephlogisticated.

*Of precipitations of and by lead.*

Metals dissolved in the vitriolic and marine acids, and precipitable by lead, according to the indication of the balance of affinities, are yet slowly precipitated, because the first portions of lead that are dissolved form salts of difficult solution, which cover its surface, and protect it from the further action of the acid ; and yet it contains so little phlogiston, that a great deal of it must be dissolved before it gives out enough to precipitate the dissolved metals.

Mr. BERGMAN observed, that a very saturate solution of lead is difficultly, if at all, precipitable by iron. Does not this also arise from some lead being taken up in its metallic form ? Iron does not precipitate lead from the marine acid, though a  
pre-

precipitate appears; for this precipitate still retains the marine acid: on the contrary, lead precipitates iron from this acid, though very slowly.

*Of precipitations of and by mercury.*

Though the difference betwixt the quiescent and divellent powers be very small, yet mercury is quickly precipitated from the vitriolic acid by copper; because the attraction of the calx of mercury to phlogiston is very strong, and a very small proportion of that contained in copper is sufficient to revive it.

Silver does not precipitate mercury from the vitriolic acid, unless it contains copper, and then it does precipitate it; yet if silver and turpeth mineral be distilled, the mercury will pass in its metallic form, WENZEL 42.; which shews that the affinity of calx of mercury to phlogiston is increased by heat. The difference betwixt the quiescent and divellent powers is indeed very small.

Silver appeared to me to precipitate mercury from the nitrous acid, though very slowly, when the solution of mercury was made with heat, and not over saturated; but when the solution of mercury was made without heat, it was not at all precipitated. On the other hand, mercury precipitates silver from this acid, not by virtue of the superiority of the usual divellent powers, but by reason of the attraction of mercury and silver to each other, for they form partly an amalgama and partly vegetate, and scarce any of either remains in the solution. The same thing happens, that is, they vegetate, if solutions of both metals in the same acid be mixed together.

Silver does not precipitate mercury from the solution of sublimate corrosive; but, on the contrary, mercury precipitates silver from the marine acid: and if a solution of horn silver in volatile alkali be triturated with mercury, the silver  
will

will be freed from its acid and calomel formed, 1 MARGRAAF 284.; and yet, if calomel and silver be distilled, the mercury will pass in its metallic form, and horn silver will be formed, *ibid.* 286. The same thing happens if silver and sublimate corrosive be distilled, 1 POTT. 338. STAHL *des sels*, 306; the affinity of calx of mercury to phlogiston increasing with the heat.

*Of precipitations of and by bismuth.*

With respect to the vitriolic acid I have made the sum of the quiescent and divellent powers equal, though in fact sometimes the one preponderates and sometimes the other. Wismuth precipitates nothing from vitriol of copper in 16 hours; nor does copper from vitriol of wismuth. Copper is said to precipitate wismuth from the nitrous acid; but I have also seen copper precipitated from this in its metallic form by wismuth. The variations proceed from the different dephlogistication of copper.

*Of precipitations of and by nickel.*

Unless nickel be pulverised it scarcely precipitates any metal.

Zinc precipitates a black powder from the solution of nickel in the vitriolic and nitrous acid, which Mr. BERGMAN, by a method peculiar to him, has shewn to consist of arsenic, nickel, and a little of the zinc itself. The arsenic attracting the calx of nickel\*; but zinc precipitates nickel from the marine acid.

The solution of iron in vitriolic acid acts on nickel, and that of nickel in this same acid acts on iron; but neither precipitates the other in 24 hours; but on longer rest, iron seems to have the advantage; but iron clearly precipitates nickel

\* 1 SUENSK. Handling. 1780.

from the nitrous acid; and though nickel seems also to precipitate iron, yet this arises only from the gradual dephlogistication of the iron.

Nickel precipitates copper in its metallic form from the vitriolic acid. It also precipitates copper from the nitrous and marine acids; but copper precipitates arsenic from a nitrous solution of nickel. The vitriolic and nitrous solutions of lead seem to act in specie on nickel, that is, to dissolve it without any decomposition, the calces uniting to each other. The vitriolic and nitrous solutions of nickel for some time act on lead in the same manner; but at last nickel seems to have the advantage. With regard to the marine acid, lead seems to have the advantage, though a black precipitate is seen, whichever of them is put into the solution of the other.

Nickel readily precipitates wismuth from the vitriolic and nitrous acids; but as to the marine I found each of these semi-metals soluble in the solution of the other, yet nickel precipitates wismuth very slowly, and only as to part; and wismuth precipitates a red powder, which I take to be ochre, from the solution of nickel.

Nickel and tin are slightly acted on, each by the salt of the other; but the precipitations are as indicated by the balance of affinities.

### *Of precipitations of and by cobalt.*

Cobalt is not precipitated either from the vitriolic or nitrous acid by zinc; but it seemed to me to be precipitated by zinc from the marine acid.

Though iron precipitates cobalt from the three acids, yet I found much of the cobalt retained both by the vitriolic and nitrous acids, particularly the latter, which, after letting fall

the cobalt, afterwards re-takes it, and lets fall the dephlogisticated calx of iron.

Nickel also, though it does not precipitate cobalt itself, as appears by the remaining redness of the solution, yet constantly precipitates some other heterogenous substance from it. The solution of cobalt in the marine acid becomes colourless by the addition of nickel.

Wismuth is soluble in the vitriolic and nitrous solutions of cobalt, and causes a small white precipitate, but does not affect the true cobaltic part. These solutions in vitriolic acid cannot be attributed to an excess of acid, as they are made in a dilute acid, and without heat. Copper also precipitates a white substance from the nitrous solution of cobalt, which I take to be arsenic.

It is difficult to procure either nickel or cobalt very pure; it is evident those I used were not so.

### *Of precipitations of and by regulus of antimony.*

Copper neither precipitates, nor is precipitated from, the vitriolic acid by regulus of antimony, at least in three days; but vitriol of antimony in specie dissolves it slowly.

The regulus is also acted upon by vitriol of lead, for it becomes red after remaining 16 hours in the solution of that vitriol; and lead scarcely precipitates it from the vitriolic acid.

I also found, that powdered regulus precipitates vitriol of mercury very slightly.

Wismuth neither precipitates, nor is precipitated by, this regulus from the vitriolic acid in 24 hours.

Though tin precipitates this regulus from the nitrous acid, yet if the regulus be put into a solution of tin in this acid, in 16 hours neither will be found in the solution, either  
by

by reason of the dephlogistification, or of the union of the calces to each other.

Iron does not precipitate this regulus intirely from the marine acid, but a triple salt seems to be formed, consisting of the acid and both calces. The regulus is also soluble in marine salt of iron.

Neither does copper precipitate the regulus from marine acid in 16 hours; and if the regulus be put into marine salt of copper it will be dissolved, and volatile alkalies will not give a blue but a yellowish white precipitate, so that here also a triple salt is formed.

### *Of Precipitations of and by regulus of arsenic.*

The solutions of arsenic act in most cases like two acids: thus iron, copper, lead, nickel, and zinc, are acted on by vitriol of arsenic (that is, its solution in vitriolic acid) but scarce give any precipitate.

Neither does iron precipitate arsenic from the nitrous acid, but copper does, and even silver gives a slight white precipitate; but regulus of arsenic precipitates silver completely in 16 hours. Hence the former precipitate seems to be a triple salt.

Mercury also slightly precipitates arsenic from the nitrous acid, and seems to unite to it, yet is itself precipitated by regulus of arsenic in 24 hours.

Wismuth forms a slight precipitate in the nitrous solution of arsenic; but regulus of arsenic forms a copious precipitate in the nitrous solution of wismuth; so that I believe the calces unite.

Nickel does not precipitate arsenic from the nitrous acid, but both calces unite; but regulus of arsenic produces a copious precipitate in the nitrous solution of nickel, yet the liquor continues

green ; so that certainly the nickel is not precipitated ; the white precipitate in this case seems to be slightly dephlogisticated arsenic.

This regulus also causes a white precipitate in the nitrous solution of cobalt, but the liquor still continues red.

With regard to the marine acid, copper precipitates the regulus, but volatile alkalies do not strike a blue with this solution, which shews the copper unites with the arsenic. Iron also precipitates the arsenic. Tin is soluble in marine solution of arsenic, but I could observe no precipitate, nor does regulus of arsenic precipitate tin.

Neither wismuth nor the regulus of arsenic precipitate each other from the marine acid in 16 hours. Regulus of antimony is also acted upon by the marine solution of arsenic, though it causes no precipitate, nor does the regulus of arsenic precipitate it.

